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Fundamental Parameters Contributing to Residual Lignin in Kraft Pulp

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FUNDAMENTAL PARAMETERS CONTRIBUTING TO RESIDUAL LIGNIN IN KRAFT PULP

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ABSTRACT

Recent advances in kraft pulping have improved the selectivity of this process and extended the degree of practical delignification. Despite these improvements, little is known of the nature of residual lignin for low kappa number kraft pulps. This paper examines the structure of residual lignin for seven conventional kraft (CK:kappa number 33-13) and six Lo-Solids® kraft pulps (LS:kappa number 29-11). The residual lignin in each of these pulps was isolated and characterized by ¹H NMR. The results of these analyses demonstrate that both the extent of delignification and the process employed influence the overall structure of residual lignin.

INTRODUCTION

Advances in pulping technology have continued unabated for the last decade, in response to environmental and market pressures. The ability to lower the content of lignin in kraft pulps prior to bleaching facilitates environmentally compatible bleaching practices, reduces operating costs, and may assist in the development of low effluent pulp production. The fundamental principles involved in extending kraft delignification while retaining pulp strength properties were established in the late 1970s and early 1980s (1-3). These principles include leveling out the alkali concentration, maintaining a high sulfidity particularly at the beginning of the cook, reducing the dissolved lignin concentration, and employing lower cooking temperatures. Recently, further improvements have been made in continuous modified kraft cooking technology to enhance delignification while improving pulp strength and uniformity (4-6). Despite these significant advances in pulping technology, very little is known on how changes in the kraft pulping process can influence residual lignin structure. To address this issue,

several researchers have begun to characterize the nature of residual lignin in kraft pulps (7-13). As a preliminary study in this field, we have previously reported that the functional groups of lignin can be influenced by the extent of delignification and type of pulping process employed (14). In this paper, we examine the fundamental changes in lignin structure that occur when loblolly pine is cooked under conventional and simulated Lo-Solids® kraft pulping conditions.

EXPERIMENTAL PROCEDURES

Kraft Pulping

A single, mature, loblolly pine tree grown in the southeastern United States was employed for all pulping studies reported in this paper. The tree was debarked, chipped, and carefully screened (chip thickness on average was between 2 and 8 mm). The kraft pulping experiments were performed at Ahlstrom Machinery Corp., in Glens Falls, NY. Established procedures (4) were used to simulate CK and LS kraft pulping processes; Table 1 summarizes pulp properties and conditions used.

Residual Lignin Isolation and Characterization

Residual lignin was isolated from the various pulps by employing an aqueous acidic-dioxane solution following literature procedures (10). This procedure afforded, on average, 55% yield of residual lignin. Lignin samples were then analyzed by quantitative ¹H NMR following the procedure described by K. Lundquist (15). The lignin samples were dissolved in anhydrous DMSO-d₆; pentafluorobenzaldehyde (or sodium-3-trimethylsilyl propionate-2,2,3,3-D₄) was added as an internal standard, and all NMR analyses were accomplished using a Bruker 400 MHz DMX spectrometer employing a $\pi/2$ pulse, 25-sec delay, 12,000 Hz sweep width, and 240 transients.

RESULTS AND DISCUSSION

Cooking Results

To minimize experimental variations due to the wood source, a single wood sample was used for all the studies described in this paper. To fully explore the dependency of lignin structure on kraft pulping process type, we elected to prepare a series of CK and LS kraft pulps covering a kappa number range of 39.3-11.0. Table 1 provides a brief description of the physical properties of these kraft pulps.

The data in Table 1 clearly demonstrate that extended modified continuous cooking procedures can attain lower lignin content pulps while retaining higher viscosity values. Our interest in these pulps was twofold. First, we were interested in determining if pulps of differing lignin contents would have differing types of lignin structures. Second, we were interested in establishing if differences in pulping technology such as those found between conventional and Lo-Solids® would also impact lignin structure. To examine these issues, the residual lignin from kraft pulps CK33-13 and LS29-11 were isolated and characterized by NMR. Following literature methods, residual lignin was extracted from each of these pulps by employing an acidic dioxane solution. After purification, typical yields were in the range of 45-65%. The lignin isolated from the kraft pulps was then characterized by employing quantitative ^1H NMR methods that have been developed by Lundquist (15). Figure 1 provides a representative spectrum of a lignin sample analyzed by proton NMR.

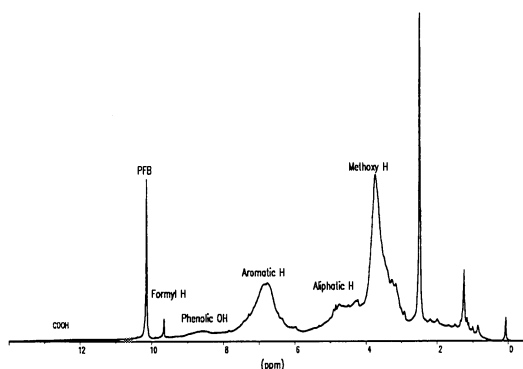


Figure 1. Quantitative ^1H -NMR spectrum of lignin samples.

The analysis of lignin structure by NMR is well described in the literature and provides a facile means for characterizing a variety of functional groups of lignin, including acid groups, and methoxy, phenoxy, and aliphatic units. The results of these analyses for the 13 pulps studied in this paper are summarized in Figures 2-5.

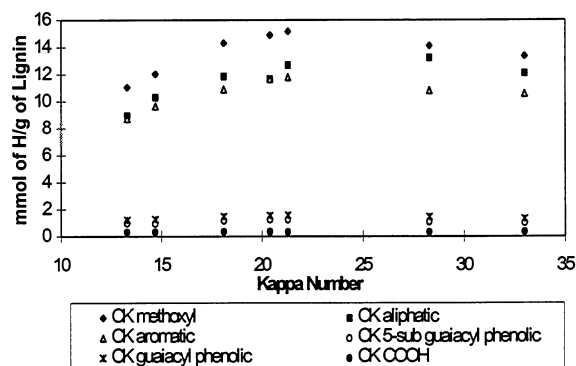


Figure 2. Content of different structural moieties in lignin samples isolated from CK pulps as determined by ^1H NMR.

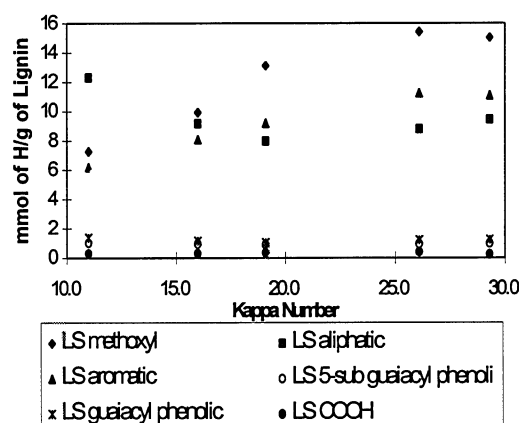


Figure 3. Content of different structural moieties in lignin samples isolated from LS pulps as determined by ^1H NMR.

It is clear from these studies that for both conventional (CK) and modified (LS) kraft pulps the content of methoxy and aromatic hydrogens in residual lignin decreases as the extent of delignification is increased. For the CK pulps, the aliphatic and guaiacyl units also decrease as delignification proceeds. In contrast, for the LS pulps, the aliphatic and guaiacyl units appear to be at a minimum value for the K17 pulp. The lignin acid groups for both the CK and LS pulps remain approximately constant.

A comparison of the structural groups of residual lignins from the LS and CK kraft pulps provides additional information on the nature of kraft pulping and the influence that process modifications can have on the final product.

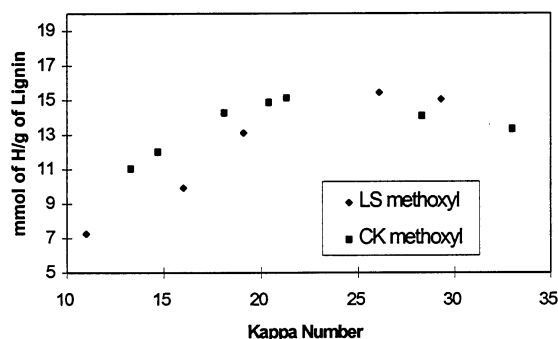


Figure 4. Changes in methoxy content of residual lignin samples isolated from LS and CK pulps as determined by ^1H NMR.

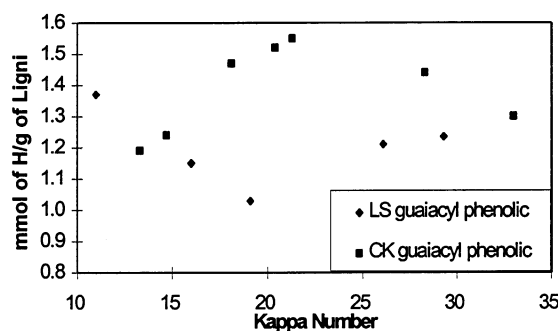


Figure 5. Changes in guaiacyl content of residual lignin samples isolated from LS and CK pulps as determined by ^1H NMR.

As shown in Figure 4, the content of methoxy groups was found to be lower in the modified kraft than in the conventional kraft pulps. The guaiacyl and 5-substituted guaiacyl units of the conventional and modified kraft pulps (see Fig. 5) exhibited a more complex pattern. At high kappa values, both the conventional and modified kraft pulps (ca. 30 kappa number) have comparable levels of phenoxy groups, but as delignification is extended, the LS pulps exhibit a decrease in free phenols whereas the conventional has an increase. Finally, at low kappa levels (<15), the extended modified pulps appear to have higher contents of free phenols. We have previously noted (14) a comparable pattern of residual lignin when comparing a conventional kraft pulp with an EMCC pulp. These differences in lignin structure were attributed to differing amounts of β -O-aryl ethers present in the pulp as delignification proceeds due to the differences in pulping.

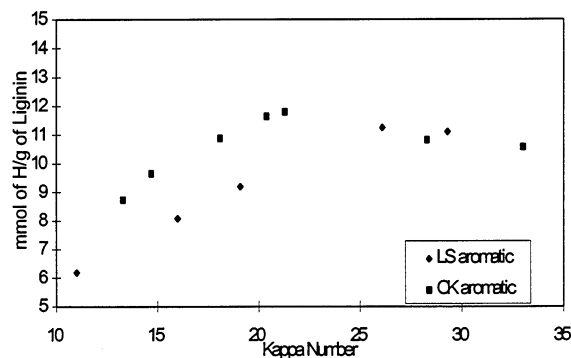


Figure 6. Changes in aromatic proton content of residual lignin samples isolated from LS and CK pulps as determined by ^1H NMR.

Figure 6 shows that there is a decrease in aromatic proton character in residual lignin as delignification is increased from the kappa ~30 pulps to kappa 11 pulps. Furthermore, as previously noted, the extended modified pulps appear to have lower amounts of aromatic protons than the conventional pulps, suggesting that they are further substituted. These results again mirror our previous results (14).

CONCLUSIONS

In summary, this paper provides further evidence that the nature of residual lignin in kraft pulps is influenced by the extent of delignification. Furthermore, we have noted that kraft pulping process parameters can influence the nature of residual lignin. All of these studies have been performed with a single wood source, and hence, variations in lignin structure due to the use of commercial samples have been eliminated. Our results continue to suggest that the kraft pulping process has a tremendous influence on the nature of residual lignin, and as our understanding of this process is increased, we anticipate that it will become possible to design kraft pulp processes to optimize subsequent bleaching operations.

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	Conventional Kraft Pulps							Lo-Solids® Kraft Pulps					
Pulp	CK33	CK28	CK21	CK20	CK18	CK15	CK13	LS29	LS26	LS19	LS17	LS16	LS11
Kappa #	33.0	28.3	21.3	20.4	18.1	14.7	13.3	29.3	26.1	19.1	17.1	16.0	11.0
Viscosity mPa	32.6	24.8	22.6	22.4	18.5	13.3	13.1	43.4	36.1	25.5	21.1	19.2	12.1
Total Yield % on Wood	48.6	48.1	46.6	47.4	46.8	44.7	44.0	48.3	47.8	45.6	44.9	44.2	41.8
Max. Temp °C	168	170	170	170	171	171	171	160	163	166	169	170	170
H-Factor	1201	1213	1999	2311	2987	3496	3499	2003	2442	3362	4126	4489	4474
Total EA Consumed % on wood NaOH	14.8	14.0	15.4	14.9	15.3	16.7	16.4	14.1	15.2	15.0	15.9	16.6	17.8

Table 1. Relevant pulping conditions and pulp properties from the CK and LS pulps.

